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Durability of Diesel Particulate Filters

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OAK RIDGE NATIONAL LABORATORY
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Materials Science and Technology Division

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ABSTRACT

A substantial amount of testing and analysis was performed over the 13-year-duration of this Cooperative Research and Development Agreement (CRADA) between Cummins Inc. and the Oak Ridge National Laboratory (ORNL). ORNL's work focused on developing fundamental understanding of the mechanical and physical properties and their relationship to the microstructure of Diesel Particulate Filter (DPF) materials (i.e., cordierite, aluminum titanate, Si-SiC). These materials exhibit significant strain tolerance owing to their highly porous and mircocracked microstructures. That is, while very weak, the porous and compliant microstructure could withstand large strains without failing catastrophically. Substantial knowledge was also gained with respect to preparation of test specimens for evaluation of mechanical properties and the care required. Once the role of the microstructure of the “wall” material on its mechanical response was understood, the DPF honeycombs themselves were re-examined, and the influence of the honeycomb structure was considered. Cummins’s work focused mainly on the apparent strength of the DPF honeycomb structure and using the material properties generated at ORNL for input to their regeneration and performance-predictive models.

1. STATEMENT OF OBJECTIVES

The objectives of this CRADA were: to identify and implement test techniques to characterize the physical and mechanical properties of ceramic substrates used as diesel particulate filters (DPFs), to identify the mechanisms responsible for the progressive thermo-mechanical degradation and resultant fracture of DPFs, and to develop analyses and provide data for simulation tools for predicting the long-term reliability and durability for the DPFs under engine operating conditions. Cummins provided DPF samples that they were considering for use in the next generation of diesel truck systems for this effort, and ORNL provided a supportive role in their continued refinement. This work will ultimately contribute to improved efficiency and reduced emissions in advanced combustion engines for passenger and commercial vehicle applications through accelerated development of cost-competitive aftertreatment for vehicle applications and new or early stage enabling technologies needed to improve fuel efficiency, performance, and emissions in internal combustion engines.

ORNL possesses a long history of investigating the role of microstructural on the mechanical properties and performance of ceramic materials. ORNL was uniquely equipped to partner with Cummins in the experimental evaluation of DPFs utilizing many of the characterization tools acquired and formerly maintained by the High Temperature Materials Laboratory (HTML) Program. Unique facilities for DPF characterization at ORNL include Randy Parten’s machining expertise and laboratory and a microtesting rig coupling simple tension with measured strain using digital image correlation (DIC).

The entire length of the CRADA was 150 months. It began in June 2004 and ended in November 2016. All the tasks are described in the following.

2. BENEFIT TO THE FUNDING DOE OFFICE'S MISSION

This work was part of the EERE Vehicle Technologies Office Program and was specifically referenced as an R&D agreement in the Propulsion Materials subprogram. The subject agreement leveraged DOE funds via the in-kind contributions of Cummins and provided a path for the commercialization of technologies developed.

3. TECHNICAL DISCUSSION OF WORK PERFORMED BY ALL PARTIES

3.1 OAK RIDGE NATIONAL LABORATORY (ORNL)

ORNL provided technical R&D support to Cummins involving Cummins's own DPF materials through the above-listed Tasks. Different DPF materials were evaluated over the 150-month-long project.

The following is a brief synopsis of work conducted during the project's 150 months.

FY04 (June 2004 - September 2004):

Test techniques were identified and implemented to determine the physical and mechanical properties of DPF ceramic substrates. Specifically, values for the elastic modulus and flexural strength were determined by dynamic mechanical analysis and 4-pt bending, respectively. A round-robin testing program involving Corning, Cummins and ORNL was planned to assess the precision of test methods for the determination of strength and elastic properties. Work was conducted to implement probabilistic design methodologies and to predict the reliability and durability of DPFs when subjected to an arbitrary thermomechanical history.

FY05 (October 2004 – September 2004):

A procedure was developed to prepare test specimens from cellular DPFs to determine the fracture toughness of porous cordierite plates by the double-torsion test method. Using this test method, the fracture toughness of porous cordierite was found to decrease with temperature from 0.45 ± 0.02 MPa√m at 20°C to 0.36 ± 0.07 MPa√m at 800°C. Work was initiated to determine the slow-crack growth behavior of porous cordierite and cellular structures of porous cordierite using the load relaxation variation of the double torsion test method and the constant stress-rate flexural test method according to ASTM C1465, respectively. The results from these tests enabled the prediction of service life of porous cordierite DPFs. A round-robin testing program was completed to assess precision in the determination of the 4-pt flexural strength of cordierite DPFs. It was found that the average strength and standard deviation of all tests were 6.73 and 0.83 MPa, respectively and that the repeatability and reproducibility standard deviations were 0.35 and 0.9 MPa, respectively. The Weibull modulus was found to be 24.1.

FY06 (October 2005 - September 2006):

The fracture mechanical behavior of porous cordierite was characterized in conditions relevant to the operation of DPFs. It was observed that the temperature dependence of fracture toughness was unusual, in that the fracture toughness values increased with temperature above 500°C. The amorphous phase at the grain boundary was characterized and found to be responsible for the increase in fracture toughness of porous cordierite at elevated temperature. Additional physical and mechanical property measurements were carried out to better understand the time-dependent, spatial, and fracture mechanical behavior of DPF substrates.

FY07 (October 2006 - September 2007):

A comprehensive fracture mechanics based investigation was conducted for porous cordierite. Fracture toughness and slow crack growth tests were performed in the double-torsion test geometry for the service temperature range of 20-900°C. The elastic properties of the filter wall substrate were characterized with resonant ultrasound spectroscopy (RUS) in the temperature range of 20-1000°C. The developed test procedures were employed to rank the relative thermal shock resistance of several candidate DPF substrate materials. The properties utilized to measure the thermal shock resistance included the fracture toughness, elastic modulus, and the coefficient of thermal expansion. NDE techniques were developed for detecting the integrity of DPFs.

FY08 (October 2007 - September 2008):

Mechanical and thermal shock characterization test procedures were employed to rank the relative thermal shock resistance of several candidate DPF substrate materials. The properties utilized to measure the thermal shock resistance included the fracture toughness, elastic modulus, and the coefficient of thermal expansion. For cordierite substrates, the porosity of the substrate was the most important variable that determined the elastic and fracture mechanical properties of the substrate. The effect of porosity on the fracture toughness of cordierite substrates was quantitatively identified. In addition, the effect of catalytic washcoat loading on the high temperature elastic properties of DPF substrates was characterized. A field-returned DPF was thoroughly characterized and its properties were compared to those of unused and uncoated filters. The differences in the properties of field returned filters were explained based on microstructural observations.

FY09 (October 2008 - September 2009):

Mechanical and thermal shock characterization test procedures developed earlier were employed to measure properties of cordierite, aluminum titanate, and mullite DPFs. In ASTM round robin testing, the strength of SiC DPF materials was found to be greater than 3x than that of cordierite. Correcting the results for the moment of inertia for a honeycomb structure resulted in a factor of 2x for all strengths. The Young's modulus of the aluminum titanate varied from the core to the rim with the rim region being stiffer. Finally, dynamic fatigue testing showed that the mullite DPF material has excellent resistance to slow crack growth in ambient air. The aluminum titanate material exhibited significant variability in strength, which required additional testing before a conclusion can be drawn.

FY10 (October 2009 - September 2010):

Mechanical and thermal shock characterization test procedures developed earlier were employed to measure properties of cordierite, aluminum titanate, and mullite DPF materials, with particular emphasis on aluminum titanate. Its microstructure is porous and microcracked with more prismatic grains, while cordierite possessed more plate-like grains. The Al_2TiO_5 DPF material has higher coefficient of thermal expansion than that of the cordierite DPF. The Al_2TiO_5 DPF material has lower strength than that of the cordierite DPF. No strong trends suggesting evidence of slow crack growth at ambient or elevated temperatures were observed.

FY11 (October 2010 – September 2011):

Mechanical and thermal shock characterization test procedures were employed to measure properties of Si-SiC DPF materials. The properties and microstructure of this material were compared to those of cordierite and Al_2TiO_5 DPF materials. The fracture toughness of the Si-SiC DPF was measured using the double torsion technique and found to increase from room temperature to 500°C. The fracture strength was measured as a function of stressing rate, sample size, and temperature; the strength was also observed to increase with temperature. The mechanism for the increase in fracture toughness and flexural strength with temperature is thought to be related to the softening of free silicon (Si) in the reaction-bonded SiC. The importance of reliable input data was demonstrated with predictive simulations of the number of regeneration cycles to component failure.

FY12 (October 2011 – September 2012):

Continuing from last FY, the fracture toughness of the Si-SiC DPF was measured using the double torsion technique and found to increase from room temperature to 900C. The mechanism for this is thought to be related to the softening of the free Si *and/or* glassy phase. The role of microstructure on the physical and mechanical properties of porous cordierite as investigated. Temperature cycling to 1000°C led to experimental evidence of microcrack healing and reopening for the porous cordierite during cooling, which was also observed in Al_2TiO_5 DPF materials.

FY13 (October 2012 – September 2013):

The stress-strain responses of three DPF materials were examined in simple tension using a new microtesting rig whereby a DPF plate is pulled in simple uniaxial tension and the strain is measured using digital image correlation (DIC). The non-linear stress strain behavior of cordierite, Al_2TiO_5 and Si-SiC materials was a function of both the porosity and microcrack density. As the microcrack density increases the secant modulus decreases as more defects become "activated" in the load sustaining state. That is, as the load increases the DPF materials become more compliant. The characterization of the dynamic and static fatigue response of Si-SiC DPFs was also completed, and it was observed that the fracture strength increases with temperature above 600°C and with decreasing loading rate. The mechanism responsible for this behavior is believed to be the formation of a glassy phase, which fills in and heals pre-existing cracks.

FY14 (October 2013 – September 2014):

A uniaxial microtensile setup coupled with DIC was used to measure anisotropy in mechanical properties of DPF materials as well as initiate the development of a second methodology to measure the fracture toughness of porous ceramics in pure tension. Computational researchers will be able to implement the anisotropic elastic constants into current models for better lifetime prediction of long-term reliability and durability of DPFs. The single edge notched beam in tension affords the opportunity to investigate the fracture toughness without complications due to complex stress states as in the case of 3-point and 4-point bend experiments. An investigation of the mechanical properties of a next-generation filter material, zeolite, has been initiated. Further testing on current DPF materials continued so as to gain further insights into their complex mechanical behavior.

FY15 (October 2014 – September 2015):

The increase in fracture toughness with increasing temperature observed in the Si-SiC material is mostly due to the strengthening effect of the oxide layer formed at high temperature that alters, seals or joins the pre-existing cracks. Analyses of the fracture mechanics of DPF structures has begun in an effort to provide another measure of the fracture toughness from test samples that are easier to fabricate and closer to the actual product. Research on the prior test samples carefully machined from the walls of the honeycomb structure shows that although machining debris accumulates in pores, it does not have a significant impact on the properties of the contiguous portion of the sample. Further the bulk porosity does not seem to change significantly with decreasing wall thickness. Machining must therefore introduce additional microcracks into the machining damaged layers, and as the thickness of those layers becomes significant with respect to the total sample thickness, the impact of this increase is measureable in the Young's modulus.

FY16 (October 2015 – November 2016):

TBA.

3.2 CUMMINS INC.

Cummins's main technical role was to provide DPF honeycombs for testing, strength data, regeneration modeling, and research guidance. DPF materials were chosen from current production and future products for use in the next 5 years (at the time chosen). The material strength was characterized for each of the materials using the four-point flexure method that became ASTM C1674. This standard test method was developed as a complimentary activity to the CRADA so that the honeycomb structures could be reduced to simple material strength values and different materials and cell structures could be directly compared. Stress modeling utilized the strength data and thermal properties from Cummins, and elastic modulus and fracture toughness data from ORNL to determine the structure response to specific thermal inputs known to cause fracture of the honeycomb. Over the course of this work, development of the materials by the manufacturers (utilizing data made available by the CRADA) increased the thermal stress limits of the honeycomb structures. The project was focused on advancing the knowledge of the ceramic materials in highly porous, microcracked state as a honeycomb structure. As a result of the work, we understand much more about the fracture mechanisms and factors which influence survival of the structure. The models have advanced from simple 1D estimations to 3D structures capable of inclusion of asymmetric parameters.

4. SUBJECT INVENTIONS AND PUBLICATIONS

"Subject Invention" means any invention of the Contractor (UT-Battelle, LLC) or Participant (Cummins, Inc.) conceived or first actually reduced to practice in the performance of work under this CRADA.

There was one invention conceived or first reduced to practice as a consequence of the completion of this project's work: T. M. Yonushonis, R. J. Stafford, E. Lara-Curzio and A. Shyam, "Apparatus, system, and method for detecting cracking within an aftertreatment device" US Patent # 7701231, Issued April 20, 2010.

The following publications resulted from this CRADA:

1. R. C. Cooper, M. Wheeler, A. Pandey, G. Bruno, T. R. Watkins, A. Shyam, "Effect of microcracking on the uniaxial tensile response of β-eucryptite glass ceramics: experiments and constitutive model," In review in PTS.
2. R. C. Cooper, G. Bruno, Y. Onel, A. Lange, T. R. Watkins, A. Shyam, "Young's modulus and Poisson's ratio changes due to machining in porous microcracked cordierite" (JMSC-D-16-02348R2). Accepted for publication in the Journal of Materials Science.
3. A. Shyam, G. Bruno, T. R. Watkins, A. Pandey, E. Lara-Curzio, C. M. Parish and R. J. Stafford, "The effect of porosity and microcracking on the mechanical properties and thermal expansion of cordierite diesel particulate filter materials", J. Euro. Ceram. Soc. 35 [16] 4557-4566 (2015). (DOI: 10.1016/j.jeurceramsoc.2015.08.014)
4. A. Pandey, A. Shyam, T. R. Watkins, E. Lara-Curzio, R. J. Stafford and K. J. Hemker, "The Uniaxial Tensile Response of Porous and Microcracked Ceramic Materials," J. Am. Ceram. Soc. 97 [3] 899–906 (2014).
5. G. Bruno, V. O. Garlea, J. Muth, A.M. Efremov, T. R. Watkins, A. Shyam, "Microstrain Temperature Evolution in β-eucryptite Ceramics: Measurement and Model," Acta Mater. 60 4982–96 (2012).
6. A. Shyam, E. Lara-Curzio, A. Pandey, T. R. Watkins, and K. L. More, "The Thermal Expansion, Elastic and Fracture Properties of Porous Cordierite at Elevated Temperatures," J. Am. Ceram. Soc. 95 [5] 1682–91 (2012).

7. R. J. Stafford, K. Golovin, A. Dickinson, T. R. Watkins, A. Shyam, E. Lara-Curzio, "Comparison of Elastic Moduli of Porous Cordierite by the Flexure and Dynamic Test Methods," Proceedings of the 36th International Conference on Advanced Ceramics and Composites Meeting CD ROM, Wiley & The American Ceramic Society, 2012. {Also to appear in Ceramic Engineering and Science Proceedings (CESP), Volume 33, Issue 6, 2012, Advances in Bioceramics and Porous Ceramics V, R. Narayan and P. Colombo, Editor; M. Halbig and S. Mathur, Volume Editors.
8. A. Shyam, E. Lara-Curzio, T. R. Watkins and R. J. Parten, "Mechanical Characterization of Diesel Particulate Filter Substrates," J. Am. Ceram. Soc., 91 [6] 1995–2001 (2008).
9. A. Shyam, E. Lara-Curzio, H-T Lin and R. J. Parten, "Fracture Toughness of Porous Cordierite", Ceramic Engineering and Science Proceedings, vol. 27, no. 2, pp. 75-81, 2007.
10. A. Shyam and E. Lara-Curzio, "The double-torsion testing technique for determination of fracture toughness and slow crack growth behavior of materials: a review" Journal of Materials Science, **41** [13] 4093-4104 (2006).

5. COMMERCIALIZATION POSSIBILITIES

There are a few ways in which the work performed during this CRADA may have commercial impact. The improved understanding of the strain tolerant microstructure and elastic behavior will have long term impacts on regeneration schemes for diesel engines. Second, the design of a zeolite based DPF could provide a DPF with inherent catalytic activity, combining two functions into one device.

6. PLANS FOR FUTURE COLLABORATIONS

Should follow-on work be pursued by Cummins, Inc., then there is a likelihood that ORNL will continue to provide support to Cummins.

7. CONCLUSIONS

The microstructural, mechanical, thermal and crystallographic characterizations performed by ORNL helped Cummins, Inc. to refine their regeneration schemes thusly improving the fuel economy.